Titration syntheses of polyaminosubstituted phthalocyanines *via* nucleophilic aromatic substitutions on zinc(II) 1,2,3,4,8,9,10, 11,15,16,17,18,22,23,24,25-hexadecafluorophthalocyanine

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ABSTRACT: Primary amines, secondary amines and tertiary butyl esters of amino acids are used as nucleophiles with zinc(II) hexadecafluorophthalocyanine to provide mixtures of mono and disubstituted fluorinated phthalocyanines under mild conditions, or polyaminosubstituted phthalocyanines when using the amines as solvents. Diamines give cyclic substituted phthalocyanines, binuclear or trinuclear phthalocyanines or mixtures of both types, depending on the chain length or structure of the diamine. Copyright © 2007 Society of Porphyrins & Phthalocyanines.

KEYWORDS: hexadecafluorophthalocyanine, primary amines, secondary cyclic amines, diamines, binuclear phthalocyanines.

INTRODUCTION

Phthalocyanines (Pcs) [1] have been widely used as industrial colorants, including inks, and dyes for plastics and metal surfaces [2]. More recently, applications in electronic fields such as high density information storage discs [3], liquid crystals [4], non-linear optics [5] and chemical sensors [6] have sparked intense interest in the synthesis of new phthalocyanines directed towards these applications. Most of the research from our laboratory has always been directed towards synthetic methods to produce *pure* phthalocyanines. On the other hand the patent literature is replete with preparations of *mixtures* of phthalocyanines, especially as dyes, as many applications do not require pure compounds. We have found that hexadecafluorophthalocyanines are excellent substrates to produce a wide variety of substituted phthalocyanine mixtures using many different nucleophiles, such as alcohols, phenols,

thiols, cyanide and amines [7]. Amines have been found to be highly efficient nucleophiles in nucleophilic aromatic substitution reactions on zinc(II) hexadecafluorophthalocyanines (1) [8]. As opposed to alcohols and thiols, amines usually exhibit sufficient reactivity to substitute fluorines on the peripheral and non-peripheral sites around the macrocycle of a Pc without an activating base. Another great advantage of using amines as nucleophiles is that in many cases the amine itself can be used as a solvent for the reaction. This is especially useful when higher substitution degrees are desired since performing the reaction using the nucleophile as solvent provides the highest concentration possible.

EXPERIMENTAL

Method I

Zinc(II) hexadecafluorophthalocyanine (1) and one of the amines 2-4 were mixed in a 1:1 ratio. For this purpose the Pc was partially dissolved in hot tetrahydrofuran (THF) and the amine was added as a

diluted THF solution. The reactions were conducted over a period of 48 h in refluxing THF. The products were purified by flash silica gel chromatography using ethyl acetate as the eluent.

Method II

A 26-fold excess of tertiary butyl esters of aminoacids (5-6) were treated with excess NEt_3 in THF prior to adding zinc(II) hexadecafluorophthalocyanine (1) and refluxing the mixture for 3 days. The product was then dissolved in ethyl acetate and washed with water and brine. Further purification was performed by chromatography on neutral alumina (activity grade V) using a mixture of hexanes/ethyl acetate = 3:2.

Method III

Zinc(II) hexadecafluorophthalocyanine (1) was dissolved in 3 mL of one of the amines 2-4 and then stirred over a period of 24 h at RT. The products were purified by placing the crude mixture on a flash silica gel chromatography column and eluting with ethyl acetate (excess amine remains on the silica).

Method IV

This was the same as method III with the exception that the reaction was conducted at 80 °C.

All the dark purple phthalocyanine mixtures did not melt up to 300 °C.

Preparation

Pc 7 by method I (mono- and dibutylamino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 918, 970. UV-vis (THF): λ_{max}, nm 350, 672, 656 (log ε = 4.2). ^{1}H NMR (pyridine-d5): δ, ppm 4.2 (bm), 2.4 (s), 1.7 (bm), 0.9 (bm), 0.3 (bm). ^{19}F NMR (pyridine-d5): δ, ppm -134 (s), -141 (m), -152 (m). Anal. calcd. (%) for $C_{32}N_8F_{16}Zn$ (start. mat.): C 44.39, H 0.0, N 12.95, for $C_{36}H_{10}N_9F_{15}Zn$ (mono-substitution): C 47.06, H 1.09, N 13.73, for $C_{40}H_{20}N_{10}F_{14}Zn$ (di-substitution): C 49.31, H 2.01, N 14.39, for $C_{44}H_{30}N_{11}F_{13}Zn$ (tri-substitution): C 51.56, H 2.93, N 15.04. Found: C 49.69, H 2.25, N 13.12.

Pc 7 by method III (multibutylamino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 1024, 1078, 1130. UV-vis (acetone): λ_{max}, nm 346, 686 (log ε = 4.8). ^{1}H NMR (chloroform-d1): δ, ppm 3.5-4.1 (bm), 0.8-2.2 (bm). ^{19}F NMR (pyridine-d5): δ, ppm -135 (bm), -142 (bm), -148 (bm), -152 (bm). Anal. calcd. (%) for $C_{44}H_{30}N_{11}F_{13}Zn$ (tri-substitution): C 51.56, H 2.93, N 15.04, for $C_{48}H_{40}N_{12}F_{12}Zn$ (tetra-substitution): C 53.39, H 3.68, N 15.58, for $C_{52}H_{50}N_{13}F_{11}Zn$ (penta-substitution): C 55.22, H 4.42, N 16.12. Found: C 54.36, H 3.43, N 15.29.

Pc 7 by method IV (multibutylamino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 1131, 1182, 1235.

Pc 8 by method I (mono- and dicyclohexylamino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z: 943, 1022. UV-vis (THF): λ_{max}, nm 296, 348, 658, 674 (log ε = 4.5). ^{1}H NMR (pyridine-d5): δ, ppm 4.1 (t), 2.3 (m), 1.3 (m), 0.9 (m), 0.3 (m). ^{19}F NMR (pyridine-d5): δ, ppm -140 (m), -152 (m). Anal. calcd. (%) for $C_{32}N_8F_{16}Zn$ (start. mat.): C 44.39, H 0.0, N 12.95, for $C_{38}H_{12}N_9F_{15}Zn$ (mono-substitution): C 49.28, H 1.85, N 12.94, for $C_{44}H_{24}N_{10}F_{14}Zn$ (di-substitution): C 53.18, H 3.32, N 12.93. Found: C 49.47, H 2.22, N 13.51.

Pc 8 by method III (multicyclohexylamino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 1023, 1101, 1180, 1259. UV-vis (acetone): λ_{max}, nm 348, 688 (log ε = 4.7). ^{1}H NMR (chloroform-d1): δ, ppm 0.5-2.2 (bm). ^{19}F NMR (pyridine-d5): δ, ppm -135 (bm), -140 (bm), -150 (bm). Anal. calcd. (%) for $C_{44}H_{24}N_{10}F_{14}Zn$ (di-substitution): C 51.61, H 2.35, N 13.69, for $C_{50}H_{36}N_{11}F_{13}Zn$ (tri-substitution): C 54.45, H 3.27, N 13.97, for $C_{56}H_{48}N_{12}F_{12}Zn$ (tetra-substitution): C 56.90, H 4.06, N 14.23, for $C_{62}H_{60}N_{13}F_{11}Zn$ (penta-substitution): C 59.05, H 4.76, N 14.44. Found: C 53.28, H 3.10, N 13.25.

Pc 8 by method IV (multicyclohexylamino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 1180, 1259, 1338, 1417.

Pc 9 by method I (mono-, di- and tripyrrolidinosubstituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 916, 967, 1018. UV-vis (THF): λ_{max}, nm 286, 348, 684 (log ε = 4.6). ^{1}H NMR (pyridine-d5): δ, ppm 4.2 (bm), 3.6 (t), 2.3 (bm), 2.1 (bm), 1.6 (m). ^{19}F NMR (pyridine-d5): δ, ppm -128 (s), -142 (m), -154 (m). Anal. calcd. (%) for $C_{32}N_8F_{16}Zn$ (start. mat.): C 44.39, H 0.0, N 12.95, for $C_{36}H_8N_9F_{15}Zn$ (mono-substitution): C 47.16, H 0.87, N 13.76, for $C_{44}H_{24}N_{10}F_{14}Zn$ (di-substitution): C 49.52, H 1.62, N 14.45, for $C_{44}H_{24}N_{11}F_{13}Zn$ (tri-substitution): C 51.87, H 2.36, N 15.13. Found: C 49.25, H 1.23, N 13.27.

Pc 9 by method III (multipyrrolidino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 1171, 1222, 1274, 1180, 1259. UV-vis (acetone): λ_{max}, nm 360, 762 (log ε = 4.8). ^{1}H NMR (chloroform-d1): δ, ppm 4.0 (bm), 2.0-2.4 (bm), 1.4 (s), 1.3 (s). ^{19}F NMR (pyridine-d5): δ, ppm -127 (bm), -145 (bm). Anal. calcd. (%) for $C_{56}H_{48}N_{14}F_{10}Zn$ (hexa-substitution): C 57.39, H 4.10, N 16.74, for $C_{60}H_{56}N_{15}F_9Zn$ (hepta-substitution): C 58.86, H 4.57, N 17.17, for $C_{64}H_{64}N_{16}F_8Zn$ (octa-substitution): C 60.33, H 5.03, N 17.60. Found: C 60.14, H 4.94, N 17.22.

Pc 9 by method IV (multipyrrolidino substituted fluorinated zinc(II) phthalocyanine). LDI-MS: m/z 1273, 1325.

Pc 10 by method II (ZnPc-GlyOtBu). LDI-MS: m/z (relative intensity) 974 [M]$^+$ (100), 919 [M-C$_4$H$_8$]$^+$ (25). UV-vis (THF): λ_{max}, nm 342, 678, 686, 712 (log $\varepsilon = 4.6$). ^{1}H NMR (acetone d-6): δ, ppm 5.0 & 4.7 (bs, 2H), 1.6 & 1.5 (bs, 9H). ^{19}F NMR (pyridine-d5): δ, ppm -142 (bm), -156 (bm). IR (KBr): ν, cm^{-1} 1736 (C=O), 2889 (CH). Anal. calcd. (%) for C$_{38}$H$_{12}$N$_9$F$_{15}$Zn (mono-substitution): C 46.72, H 1.23, N 12.91, for C$_{44}$H$_{24}$N$_{10}$F$_{14}$Zn (di-substitution): C 48.57, H 2.21, N 12.88. Found: C 48.12, H 1.95, N 12.91.

Pc 11 by method II (ZnPc-ProOtBu). LDI-MS: m/z (relative intensity) 1009 [M-C$_4$H$_9$O$_2$, C$_4$H$_9$]$^+$ (80), 960 [M-C$_4$H$_9$]$^+$ (140), 914 [M-C$_5$H$_{10}$O$_2$]$^+$ (720). UV-vis (THF): λ_{max}, nm 246, 352, 644, 672, 712 (log ε = 4.6). ^{1}H NMR (pyridine-d5): δ, ppm 3.8 (t, 1H), 3.1 (q, 1H), 2.8 (q, 1H), 2.0 (m, 1H), 1.6 (m, 1H), 1.5 (s, 9H). ^{13}C NMR (pyridine-d5): δ, ppm 60.8, 47.4, 47.1, 30.3, 30,1, 27.0, 25.5. ^{19}F NMR (pyridine-d5): δ, ppm -142 (bm), -152 (bm). IR (KBr): ν, cm^{-1} 1730 (C=O), 2926 (CH$_2$). Anal. calcd. (%) for C$_{41}$H$_{16}$N$_9$F$_{15}$Zn (mono-substitution): C 48.43, H 1.57, N 12.40, for C$_{50}$H$_{32}$N$_{10}$F$_{14}$Zn (di-substitution): C 51.41, H 2.74, N 12.00. Found: C 50.42, H 2.08, N 12.22.

Zinc(II) mono-(1,12-diaminododecyl)tetradecafluorophthalocyanine (14,16,18), zinc(II) di-(1,12-diaminododecyl)dodecafluorophthalocyanine (20). Zinc(II) hexadecafluorophthalocyanine (1) and 1,12-diaminododecane (12) were mixed in a 1:1 ratio. For this purpose zinc(II) hexadecafluorophthalocyanine (50 mg, 0.058 mmole) was dissolved in 4 mL THF, 1,12-diaminododecane (11.6 mg, 0.058 mmole) was added and the reaction mixture was refluxed for 2 days. After this period 50 mL of ethyl acetate were added to the crude reaction mixture. The solution was transferred to a separation funnel and washed twice with 100 mL of a 25% ethanol solution. The organic layer was collected and the solvent was removed. Further purification was achieved by silica chromatography using a 1:1 mixture of methanol and dichloromethane as the eluent. The first fraction was collected. After removing the solvent the product was obtained in 18% yield (11 mg). This amount also contained some starting material (1). UV-vis (THF): λ_{max}, nm 350, 670 (log ε = 4.4). LDI-MS: m/z 1024. ^{1}H NMR (pyridine-d5): δ, ppm 3.6 (m), 1.6 (m), 1.1-1.3 (bm), 0.8 (bm), 0.3 (bm). ^{19}F NMR (pyridine d-5): δ, ppm -140 (m), -153 (m). Anal. calcd. (%) for C$_{32}$N$_8$F$_{16}$Zn (start. mat.): C 44.39, H 0.0, N 12.95, for C$_{44}$H$_{26}$N$_{10}$F$_{14}$Zn (14,16,18): C 51.56, H 2.54, N 13.67, for C$_{56}$H$_{52}$N$_{12}$F$_{12}$Zn (20): C 56.71, H 4.39, N 14.18. Found: C 48.26, H 2.33, N 10.90

Zinc(II) mono-(1,11-diaminoundecyl)tetradecafluorophthalocyanine (15,17,19). Zinc(II) di-(1,11-diaminoundecyl)dodecafluorophthalocyanine (21). Zinc(II) hexadecafluorophthalocyanine (1) and 1,11-diaminoundecane (13) were mixed in a 1:1 ratio. For this purpose 72 mg of 1,11-diaminoundecane was

dissolved in 10 mL methanol. Meanwhile, zinc(II) hexadecafluorophthalocyanine (50 mg, 0.058 mmole) was dissolved in 4 mL THF and heated to reflux temperature (65 °C). Then the 1,11-diaminoundecane/methanol solution (0.73 mL, 0.058 mmole) was added and the reaction mixture was refluxed for 2 days. The same work-up procedure as for **14, 16, 18, and 20** was applied. The product was obtained in 17% yield (10 mg). This amount also contained some starting material (ZnF$_{16}$Pc). UV-vis (THF): λ_{max}, nm 288, 352, 646, 672 (log ε = 4.7). LDI-MS: m/z: 1010. ^{1}H NMR (pyridine-d5): δ, ppm 1.1-1.4 (bm), 0.7-0.9 (bm), 0.3 (bm). ^{19}F NMR (pyridine-d5): δ, ppm -139 (s), -153 (m). Anal. calcd. (%) for C$_{32}$N$_8$F$_{16}$Zn (start. mat.): C 44.39, H 0.0, N 12.95, for C$_{43}$H$_{24}$N$_{10}$F$_{14}$Zn (15, 17, 19): C 51.04, H 2.37, N 13.85, for C$_{44}$H$_{48}$N$_{12}$F$_{12}$Zn (21): C 56.01, H 4.15, N 14.52, found: C 69.41, H 3.21, N 11.98.

Zinc(II) mono-(1,3-diaminopropyl)tetradecafluorophthalocyanine (23,24,25), zinc(II) di-(1,3-diaminopropyl)dodecafluorophthalocyanine (26), bis zinc(II) mono-(1,3-diaminopropyl)pentadecafluorophthalocyanine (27), bis zinc(II) di-(1,3-diaminopropyl)tetradecafluorophthalocyanine (28,30), bis zinc(II) tri-(1,3-diaminopropyl)trideca-fluorophthalocyanine (29, 31, 32). Zinc(II) hexadecafluorophthalocyanine (1) and 1,3-diaminopropane (22) were mixed in a 1:1 ratio. For this purpose 0.5 mL of 1,3-diaminopropane was filled up to a volume of 50 mL with methanol. Meanwhile, zinc(II) hexadecafluorophthalocyanine (50 mg, 0.058 mmole) was dissolved in 4 mL THF and heated to reflux temperature (65 °C). Then the 1,3-diaminopropane/methanol solution (0.48 mL, 0.058 mmol) was added and the reaction mixture was refluxed for 2 days. After this period 50 mL of ethyl acetate were added to the crude reaction mixture. The solution was transferred to a separation funnel and washed twice with 100 mL of a 20% ethanol solution. The organic layer was collected. After removing the solvent the products were obtained as a blue solid in approximately 44% yield (23 mg). This amount also contained some starting material (1). UV-vis (THF): λ_{max}, nm 349, 638 (log ε = 4.7), 669 (log ε = 4.8). LDI-MS: m/z 998, 932, 1764, 1797, 1832. ^{1}H NMR (pyridine-d5): δ, ppm 1.3 (bm), 0.3 (bm). Anal. calcd. (%) for C$_{32}$N$_8$F$_{16}$Zn (start. mat.): C 44.39, H 0.0, N 12.95, for C$_{35}$H$_8$N$_{10}$F$_{14}$Zn (23, 24, 25): C 46.72, H 0.89, N 15.57, for C$_{38}$H$_{16}$N$_{12}$F$_{12}$Zn (26): C 48.87, H 1.71, N 18.01, for C$_{67}$H$_8$N$_{18}$F$_{30}$Zn$_2$ (27): C 45.58, H 0.45, N 14.29, for C$_{70}$H$_{16}$N$_{20}$F$_{28}$Zn$_2$ (28, 30): C 46.70, H 0.88, N 15.55, for C$_{73}$H$_{24}$N$_{22}$F$_{26}$Zn$_2$ (29, 31, 32): C 47.82, H 1.31, N 16.81. Found: C 48.74, H 1.38, N 14.18.

Zinc(II) mono(trans-1,2-diaminocyclohexyl)tetradecafluorophthalocyanine (34), bis zinc(II) di(trans-1,2-diaminocyclohexyl)tetradecafluo-

rophthalocyanine (**35, 36**), bis zinc(II) di(trans-1,2-diaminocyclohexyl)penta/tetradeca-fluorophthalocyanine (**37**), bis zinc(II) tri(trans-1,2-diaminocyclohexyl)tetra/tridecafluoro-phthalocyanine (**38**), bis zinc(II) tri(trans-1,2-diaminocyclohexyl)tri-decafluorophthalocyanine (**39, 40**). Zinc(II) hexadecafluorophthalocyanine (**1**) and trans-1,2-diaminocyclohexane (**33**) were mixed in a 1:2 ratio. For this purpose 0.5 mL of trans-1,2-diaminocyclohexane were diluted in 25 mL methanol. Meanwhile, zinc(II) hexadecafluoro-phthalocyanine (50 mg, 0.058 mmole) was dissolved in 4 mL THF and heated to reflux temperature (65 °C). Then the trans-1,2-diaminocyclohexane/ethanol solution (0.69 mL, 0.116 mmole) was added and the reaction mixture was refluxed for 2 days. The product was purified by silica gel chromatography using a 1:2 mixture of hexanes/ethyl acetate as the eluent. The first fraction gave the products in approximately 28% yield (15 mg). UV-vis (THF): λ_{max}, nm 344, 642 (log ε = 4.6). LDI-MS: m/z 938,

1877, 1898, 1950, 1972. ^{1}H NMR (pyridine-d5): δ, ppm 1.2-1.3 (bm), 0.8-0.9 (bm), 0.3 (bm). ^{19}F NMR (pyridine-d5): δ, ppm -139 (m), -153 (m). Anal. calcd. (%) for $C_{38}H_{12}N_{10}F_{14}Zn$ (**34**): C 48.56, H 1.28, N 14.91, for $C_{76}H_{24}N_{20}F_{28}Zn_2$ (**35, 36**): C 48.56, H 1.28, N 14.91, for $C_{76}H_{25}N_{20}F_{29}Zn_2$ (**37**): C 48.05, H 1.32, N 14.75, for $C_{82}H_{37}N_{22}F_{27}Zn_2$ (**38**): C 49.90, H 1.88, N 15.62, for $C_{82}H_{36}N_{22}F_{26}Zn_2$ (**39, 40**): C 50.41, H 1.84, N 15.78. Found: C 48.63, H 1.92, N 14.08.

RESULTS AND DISCUSSION

A wide variety of amines was tested in terms of nucleophilic aromatic substitution on fluorinated Pcs: (**A**) primary aliphatic non-cyclic amines (propylamine, butylamine, octylamine, t-butylamine), (**B**) secondary aliphatic non-cyclic amines (diethylamine, diisopropylamine, dipentylamine), (**C**) primary aliphatic cyclic amines (cyclopentylamine, cyclohexylamine), (**D**) secondary aliphatic cyclic

1
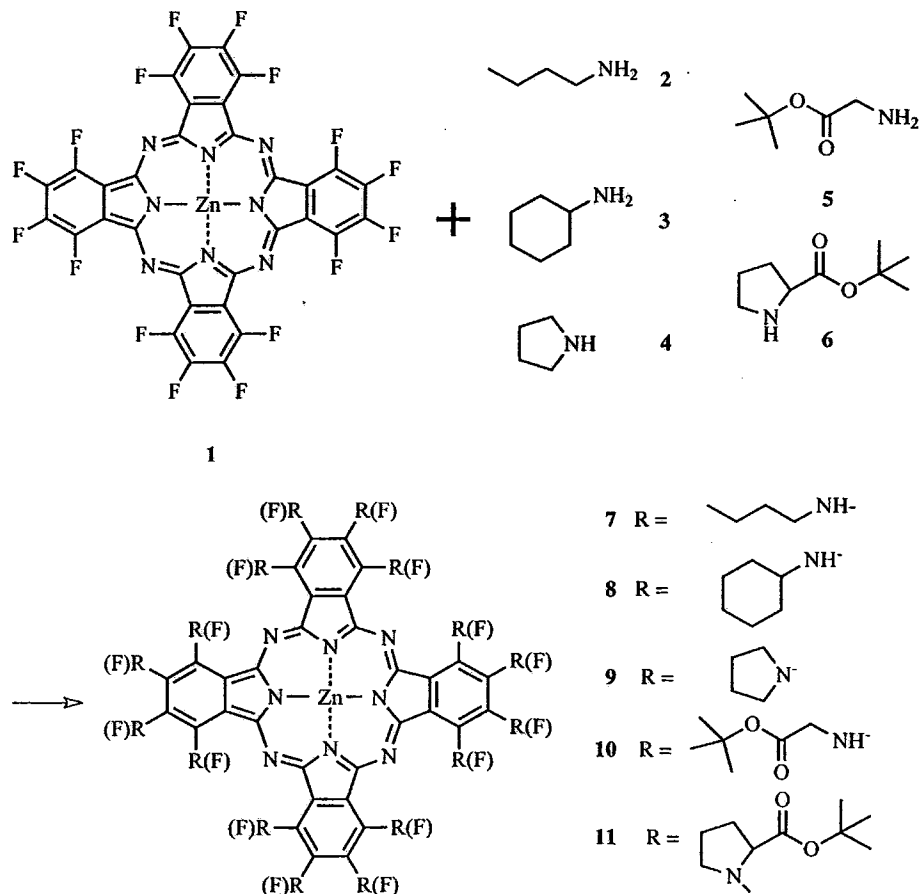
Scheme 1.

Table 1. Number of fluorines of **1** replaced by amines under different conditions

Amine	# of fluorines replaced by method I[a]	# of fluorines replaced by method II[b]	# of fluorines replaced by method III[c]	# of fluorines replaced by method IV[d]
2	0-3	---	3-5	5-7
3	0-2	---	2-5	5-7
4	0-3	---	6-8	8-9
5	---	1-2	---	---
6	---	1-2	---	---

[a]amine/Pc ratio 1:1 in reflux THF; [b]excess amine in presence of NEt$_3$ in reflux THF; [c]amine as solvent at RT; [d]amine as solvent at 80 °C

amines (pyrrolidine, piperidine, morpholine), and (**E**) aromatic amines (pyrrole, imidazole, aniline, N,N-dimethylaniline, diphenylamine).

Amines of group (**D**) were found to be the most reactive ones, closely followed by amines of group (**A**) and then (**C**). With the exception of t-butylamine which is much less nucleophilic due to its bulkiness, all of these amines reacted with fluorinated ZnPc **1** by simply dissolving the Pc in the amine and stirring the solution at room temperature. Heating the solution enhanced the nucleophilic activity of the amine causing higher numbers of fluorines to be substituted. Amines of group (**B**) did not dissolve the Pc and therefore no substitution occurred when the reaction was performed in the amine as solvent. Consequently, more stringent reaction conditions need to be applied in order to induce the nucleophilic substitution reaction. This can be achieved by heating the reaction mixture to a high temperature or by pre-forming the amino-anion by a strong non-nucleophilic base.

We expanded our studies choosing three simple amines, butylamine (**2**) representing group (**A**), cyclohexylamine (**3**) for group (**C**), pyrrolidine (**4**) for (**D**) and the teriary butyl esters of amino acids (aminoesters) tert-butyl glycine (**5**) and tert-butyl proline (**6**) to prepare Pcs **7-11** (Scheme 1).

Different reaction conditions were applied to modify the number of replaced fluorines. Mixing amines **2-4** and the Pc in a 1:1 ratio in refluxing THF (method I) gives mono- and disubstituted products (Fig. 1). To achieve the same results with aminoesters **5-6**, not only an excess of the nucleophile has to be used but it also has to be treated with the base, triethylamine (NEt$_3$), to activate the nucleophilicity of the aminoester (method II). Higher substitution degrees were obtained when amines **2-4** were used as solvents. Stirring the amine/Pc mixture at RT for 24 hours (method III) gave products with an average of 5 fluorines replaced (Fig. 2, Table 1). The reactivity was enhanced when the mixture was heated

Some interesting results were obtained when zinc(II) hexadeca-fluorophthalocyanine (**1**) was reacted with diamines of different size. It was found that the longer diamines (11 and 12 carbons, respectively) form cyclic products only (Scheme 2) while the shorter diamines (3 and 4 carbons, respectively) also form binuclear Pcs where two Pc macrocycles are connected by one or even several diamino molecules (Scheme 3, Fig. 1).

When **1** is reacted with 1,12-diaminododecane (**12**) or 1,11-diaminoundecane (**13**) in a 1:1 ratio, the main product is a Pc with two fluorines replaced by amino groups of one diamino molecule. Numerous products can be obtained by replacing some or all of the 16 possible fluorines. Both **12** and **13** have long enough chains to reach any fluorine on the macrocycle of the Pc once one amino group has been attached to it. Scheme 2 portrays three different isomers of the products, (**14, 16, 18**) (m/z = 1023.9) and (**15, 17, 19**) (m/z = 1009.8) respectively. Moreover, some formation of tetrasubstituted Pcs (**20**) (m/z = 1184.0) and (**21**) (m/z = 1155.9) occurred according to mass
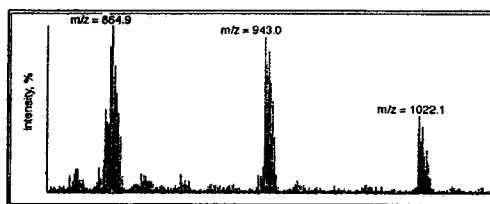
Fig. 1. LDI-MS spectrum of **8** with 0-2 cyclohexylamino substituents
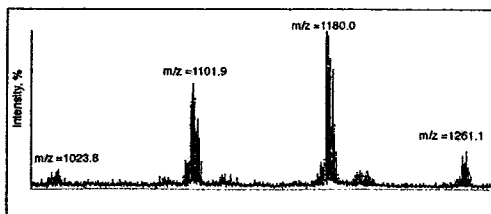
Fig. 2. LDI-MS spectrum of **8** with 2-5 cyclohexylamino substituents
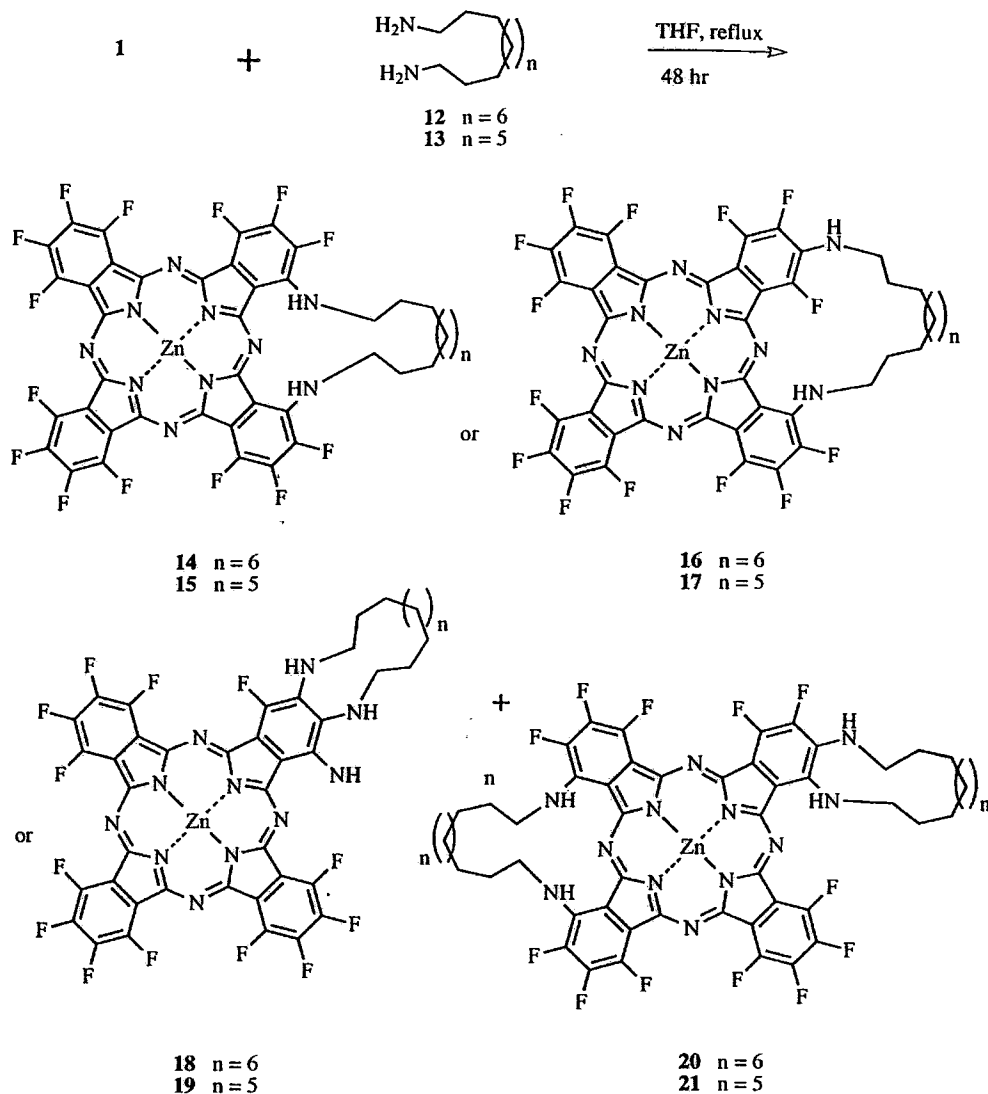
Scheme 2.

spectroscopy (Fig. 3).

When **1** is reacted with 1,3-diaminopropane (**22**) in a 1:1 ratio, the main product is, analogously to **14-19**, a Pc with one diamino molecule replacing two fluorines (m/z 897.7). The possibilities of which two fluorines get replaced are limited in this case due to the small size of the diamine. There are three possible variations (Scheme 3): **22** replaces two non-peripheral fluorines on two adjacent benzene rings **23**, or it replaces one peripheral and one non-peripheral fluorine on the same benzene ring **24**, or it replaces two peripheral fluorines on one benzene ring **25**.

The results from mass spectroscopy show some formation of a tetrasubstituted Pc (**26**) (m/z 931.8);

there is also a considerable amount of binuclear [9-11] Pcs (**27**) (m/z 1764.3), (**28, 30**) (m/z 1797.4) and (**29, 31, 32**) (m/z 1832.4) formed (Figs. 4 and 5).

Theoretically, the binuclear Pc at m/z 1797.4 can be either singly (**28**) or doubly (**30**) bridged and the Pc at m/z 1832.4 can be either singly (**29**), doubly (**31**) or triply (**32**) bridged as indicated in Fig. 5. Although the concept of mono-bridged substituted Pcs seems more realistic, it is still possible that there are doubly- and even triply-bridged binuclear Pcs. In fact, the results from experiments with longer diamines (no formation of binuclear phthalocyanines with 1,5-diaminopentane or any larger diamines but only with 1,3-diaminopropane and 1,4-diaminobutane [8],

1 + H₂N–CH₂CH₂CH₂–NH₂ $\xrightarrow{\text{THF, reflux}}$
22   48 hr

23   or   **24**

or   **25**   +   **26**
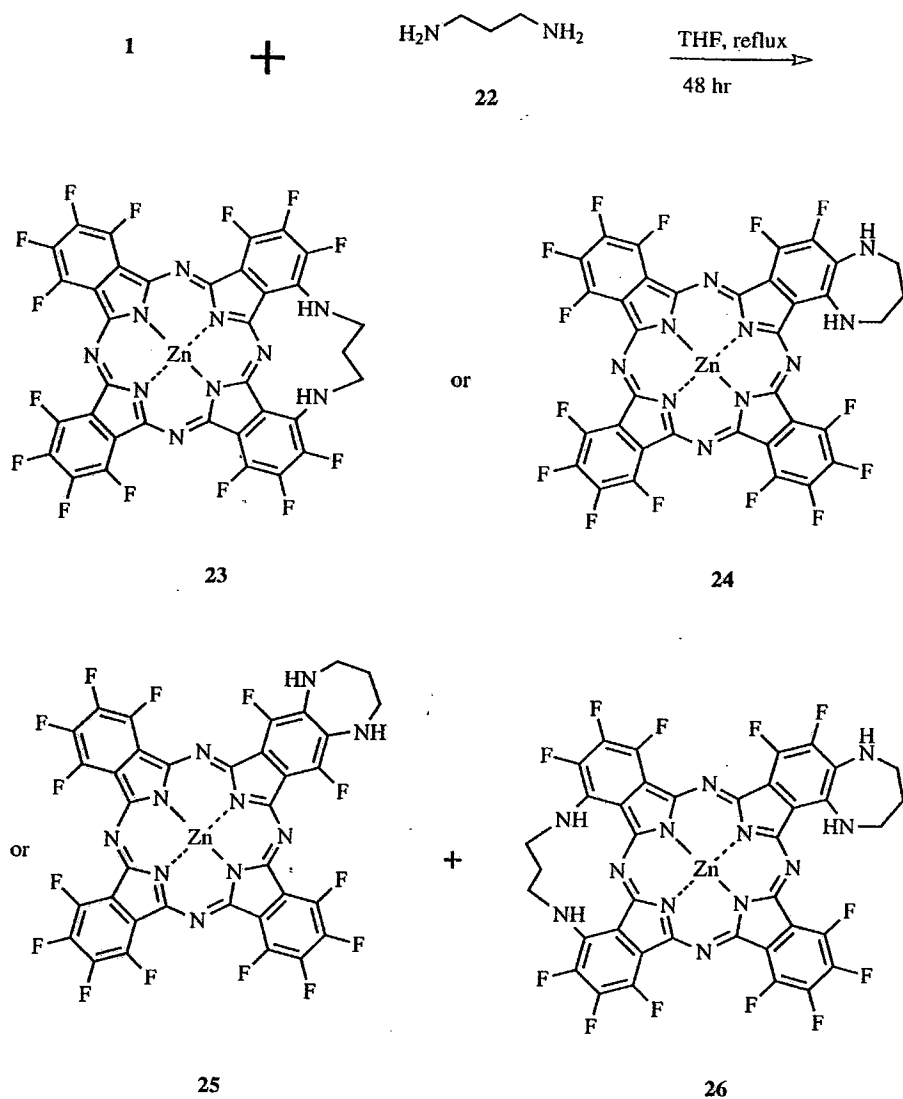
+ singly, doubly and triply bridged binuclear phthalocyanines (see Figure 1)

Scheme 3

give us a slight idea of how the binuclear Pcs are formed. Since the formation of a binuclear Pc is also observed when **1** is reacted with 1,4-diaminobutane but not with 1,5-diaminopentane or any larger diamines, it seems that bridges are only formed between two Pc molecules which are aggregated by π-π-stacking, i.e. two parallel macrocycles arranged one on top of the other (Fig. 5). The distance between such macrocycles is very likely in the range of the length of 1,4-diaminobutane or 1,3-diaminopropane.

As a result, when a diamine reacts with a Pc, the second amino group easily spans the gap to another Pc molecule which is probably aggregated to it and reacts with it. Therefore diamines, whose length is much greater than the distance between two stacked Pc molecules, do not form dimers.

Interestingly, the formation of disubstituted Pcs and of binuclear Pcs was also achieved successfully using *trans*-1,2-diaminocyclohexane (**33**) as a nucleophile.

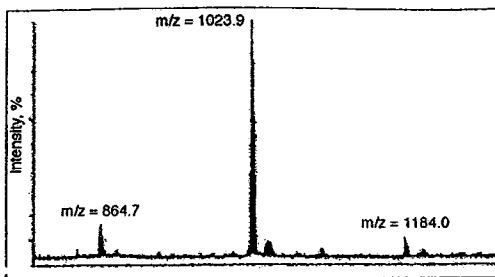The substitution leading to the main product **34**

Fig. 3. LDI-MS spectrum of 1,12-diaminododecyl substituted ZnPc mixture

of the reaction (one diamino molecule replacing two fluorines on a Pc) can occur in three different ways, just as described for **23-25**. Considering the two equilibrium forms of *trans*-1,2-diaminocyclohexane, one can easily understand that only the more stable

form (with both substituents in the equatorial position) is able to attach both amino groups to one Pc molecule as shown by the mass spectrum of the mixture (Fig. 6).

According to the mass spectrum, a number of different binuclear Pcs **(35-40)** were formed in the reaction as displayed in Scheme 4. There are two and three possible constitutional isomers respectively having the same *m/z*. It is difficult to say which isomer is more likely to be formed. However, there is no doubt that the formation of a doubly-bridged and even a triply-bridged binuclear Pc is theoretically possible, considering that the Pc macrocycles are naturally prearranged one on top of the other by π-π-stacking and even more so once they are connected by a *trans*-1,2-diaminocyclohexyl substituent. Interestingly, the UV-vis spectra of the phthalocyanine mixtures exhibit some variation in their extinction coefficients. Since substitution can occur at both the peripheral and non-
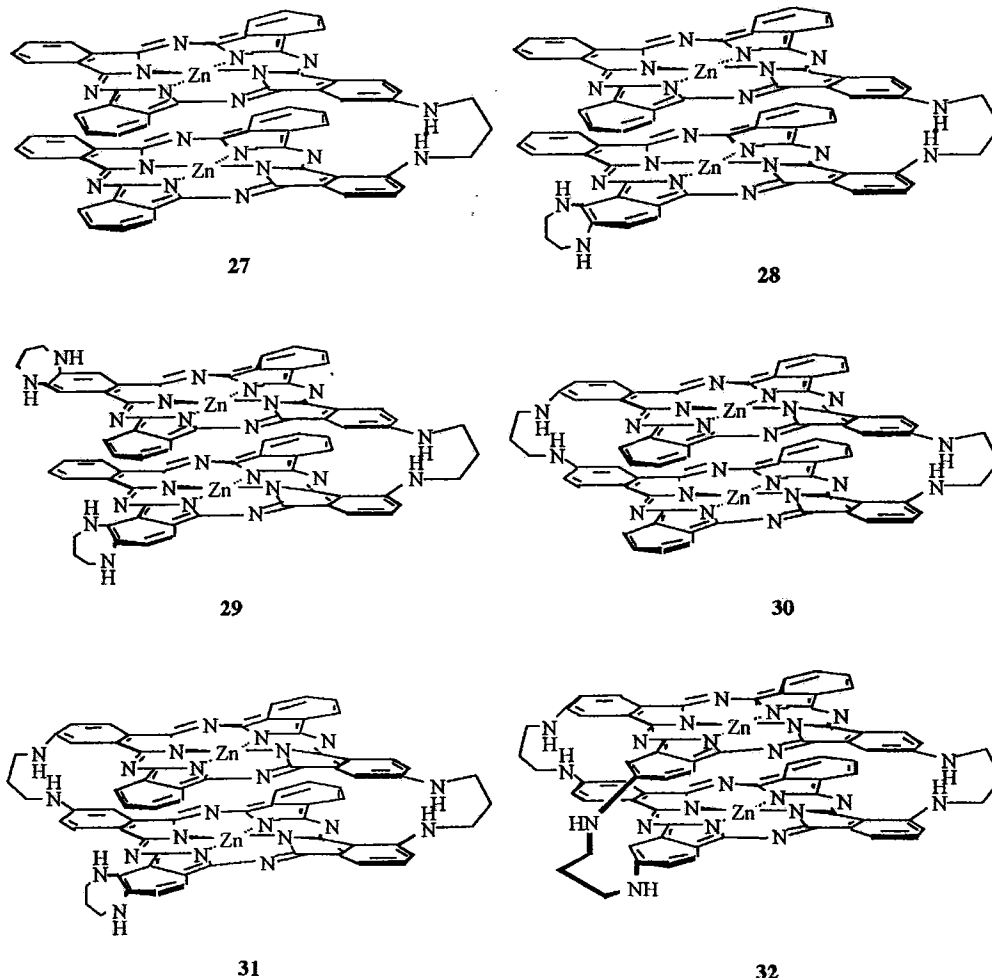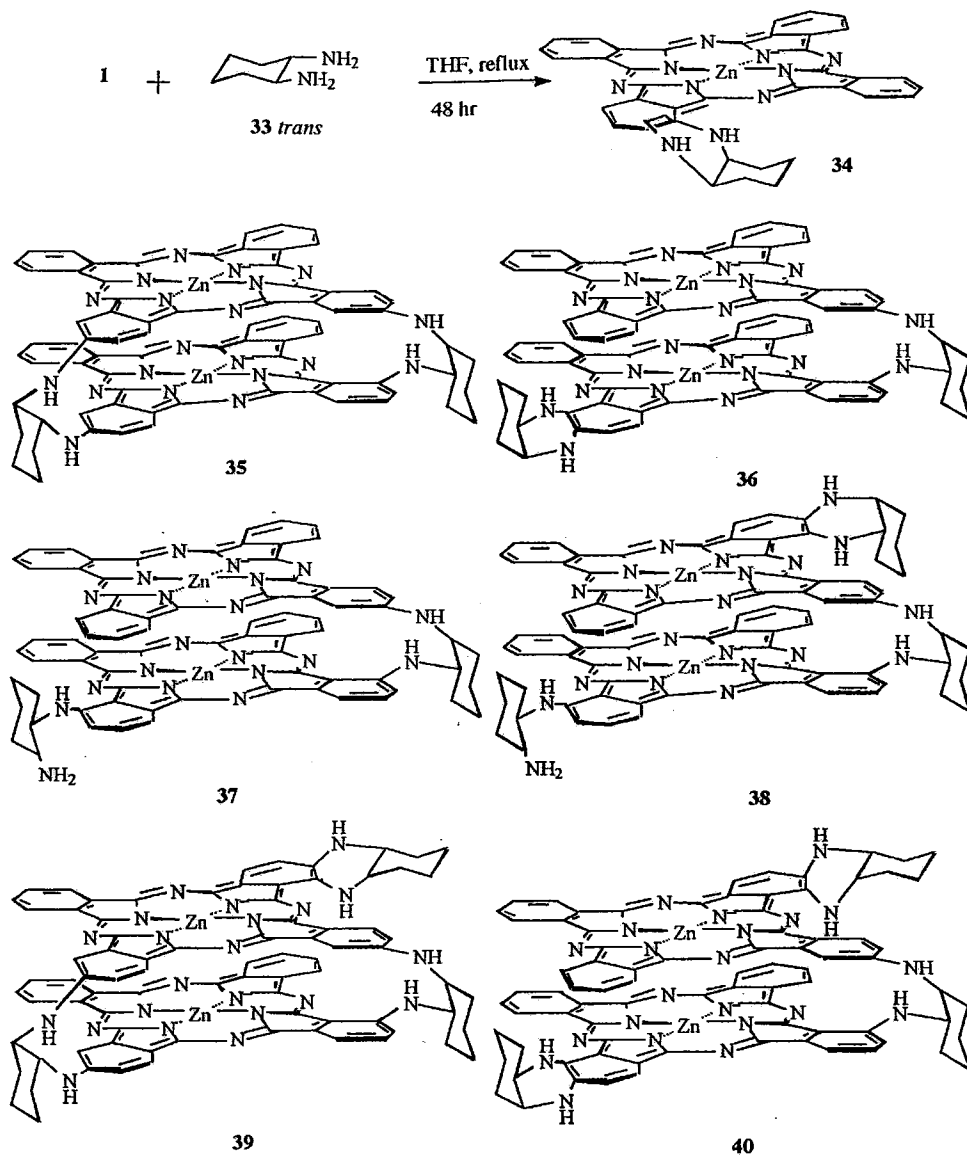

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Fig. 5. Likely structures of the 1,3-diaminopropyl substituted ZnPc mixture (fluorines omitted for clarity)
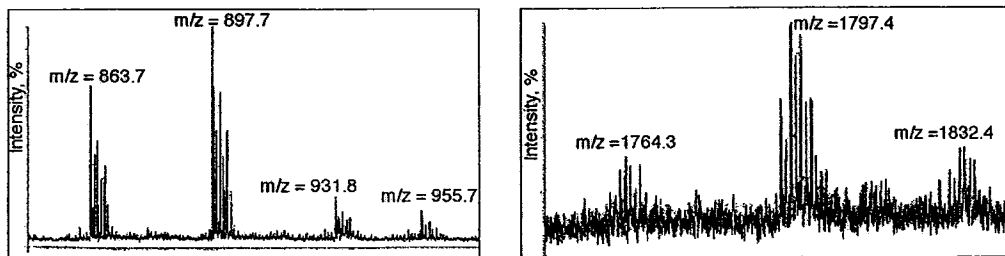
Scheme 4. (Fluorines omitted for clarity)

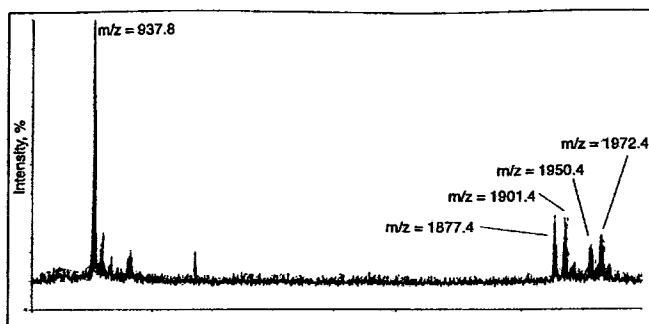Fig. 4. LDI-MS spectra of the 1,3-diaminopropyl substituted ZnPc mixture

Fig. 6. LDI-MS spectrum of *trans*-1,2-diaminocyclohexyl substituted ZnPc mixture

peripheral positions with the latter somewhat favored, there is a broadening of the absorption maximum depending on the substitution pattern of the mixture, possibly resulting in this effect.

CONCLUSIONS

Firstly, we have shown that the fluorine substituents of 1,2,3,4,8,9,10,11,15,16,17,18,22, 23,24,25-hexadecafluorophthalocyanine (1) can be easily substituted by a variety of amine nucleophiles under mild conditions to give mixtures of substituted Pcs containing 1-9 amines, depending on the reaction parameters. Thus, the properties of this mixture can be adjusted depending on the application required. Secondly, even tertiary butyl esters of amino acids can act as nucleophiles in this reaction and this observation opens the way to form polypeptide or even protein analogs, having a phthalocyanine core. Thirdly, the reaction of 1 with a variety of diamines shows that only a very narrow range of diamines, capable of forming 4-6 atom bridges are routinely possible. This observation concurs with well-known aggregation phenomena in phthalocyanines but is still unusual in its experimental verification. Finally, potential applications would depend on the cost of 1, derived from tetrafluorophthalonitrile, but the substituents as shown are introduced with negligible effort.

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